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Stereoselective preparation of *O*-alkoxy D-tetrose, D-pentose, 2-deoxy-D-glycero tetrose and 2,3-dideoxy-D-*erythro* pentose derivatives by an iterative elongation of 2,3-*O*-isopropylidene-D-glyceraldehyde

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Abstract

All D-pentoses are synthesized by one-carbon chain elongation commencing with the addition of the lithium salt of ethyl ethylthiomethyl sulfoxide to 2-*O*-(*t*-butyldimethylsilyl)-3,4-*O*-isopropylidene-D-erythrose and D-threose, **16** and **17**. The addition of the above-mentioned nucleophile to 2-deoxy-3,4-*O*-isopropylidene-D-glycero tetrose, **19**, gave rise to 2,3-dideoxy-D-glycero pentose. The starting aldehydes, **16**, **17** and **19**, are easily available from 2,3-*O*-isopropylidene-D-glyceraldehyde, **1**, and ethyl ethylthiomethyl sulfoxide.

1. Introduction

One of the goals in organic chemistry is the preparation of chiral molecules, in high chemical yields and enantiomeric excess, so that they can be used as chiral starting materials in the synthesis of more elaborate molecules.[1] In this sense, monosaccharides as well as their three- to five-carbon derivatives are especially interesting, since starting from them, a large variety of biologically interesting compounds, such as natural and non-natural sugars, antibiotics, and nucleosides, amongst many others, can be synthesized.[2] This explains the importance of finding new methodologies enabling the stereocontrolled building of 1,2- and 1,3-diols with the desired stereochemical arrangement. Synthesis of this kind of chemical structure has often been performed by transforming naturally occurring chiral compounds,[3–5] which has led to a wide range of carbohydrates. Nevertheless, this procedure does not always enable certain compounds to be obtained, either because the suitable starting material is not available or because a large number

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of synthetic steps is needed to reach them. Therefore, it is more convenient to design an asymmetric synthesis enabling the stereocontrolled building of the polyhydroxylated chain existing in the desired monosaccharide.

The methods of asymmetric synthesis which have led to the best results in monosaccharide synthesis have been the use of chiral catalysts (asymmetric epoxidation,[6–9] asymmetric dihydroxylation,[10] and enzymatic catalysis[11]), the use of chiral auxiliaries as asymmetric inductors (a chiral sulfinyl group[12] or norephedrine derivative[13]), and the use of enantiomerically pure chiral precursors,[14] controlling the formation of a new stereogenic center. Closely related to the latter category, one of the most used chiral substrates for the synthesis of monosaccharides is 2,3-*O*-isopropylidene-D-glyceraldehyde **1**, which has been reacted with a wide range of nucleophiles with the aim of elongating its hydrocarbon chain by one,[15] two,[16] or more carbon atoms,[17] which leads to tetroses, pentoses, hexoses and higher monosaccharides.

2. Results and discussion

In this paper we report the stereoselective synthesis of four- and five-carbon polyalkoxyaldehydes, by means of the consecutive one-carbon chain elongation of 2,3-*O*-isopropylidene-D-glyceraldehyde, by using commercially available ethyl ethylthiomethyl sulfoxide (EETMS) as the nucleophilic reagent.

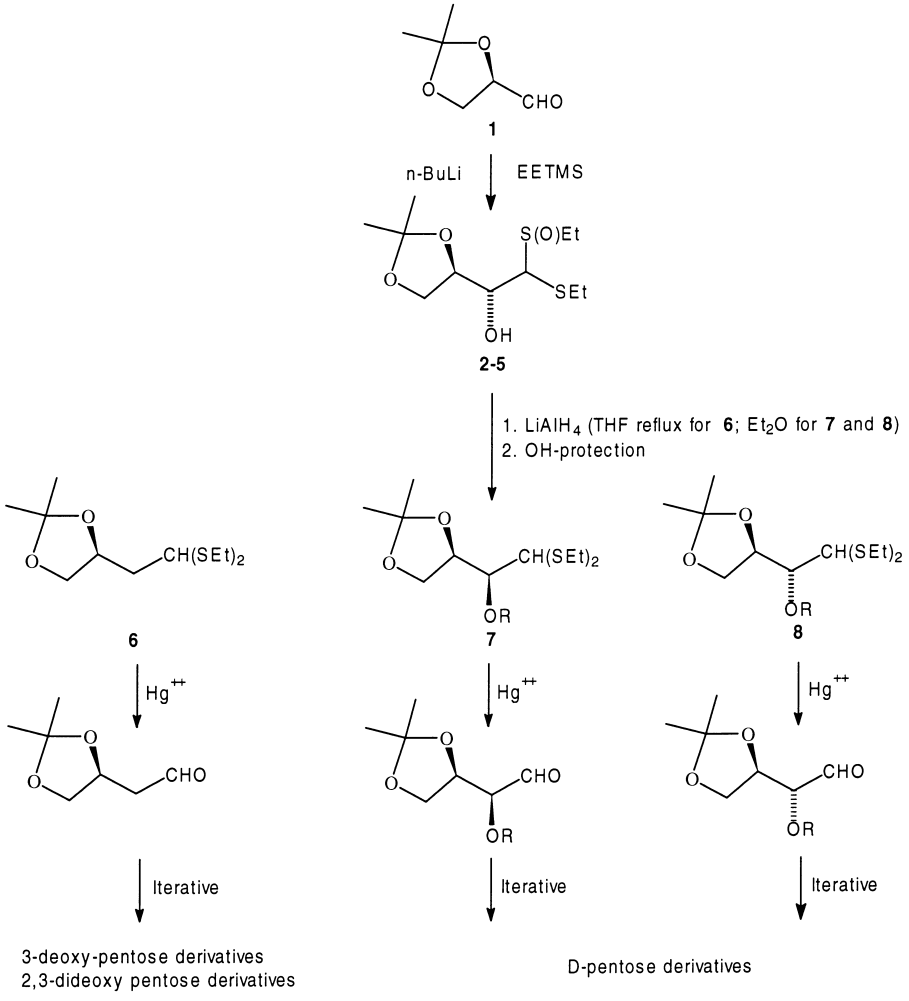
The first reaction cycle begins with addition of the lithium salt of EETMS onto aldehyde **1**, following our previously described procedure.[18] The reaction shows a high *anti*-diastereoselectivity, giving rise to D-*threo* and D-*erythro* alcohols in a 4:96 ratio, which enables a straightforward route to D-erythrose (Scheme 1). This reaction has been performed starting from 0.1 mol of aldehyde **1**, and 23 g (0.08 mol) of the diastereoisomeric mixture of D-*erythro* alcohols **2**–**5** have been easily obtained, which demonstrates that it can be scaled up as required in synthetic processes.

In order to widen the scope of this methodology to the synthesis of five-carbon polyalkoxyaldehydes, we have investigated the protection of the newly generated hydroxyl group with a variety of reagents, as well as the removal of the protecting group of the aldehyde.

The reactions aiming at the protection of the hydroxyl group, starting from α-hydroxydithioacetal mono-*S*-oxides **2**–**5** in the presence of benzylbromide, 3,4-dihydro-2*H*-pyran and *t*-butyldimethylsilyl chloride, did not give rise to the desired products. The use of the two latter protection reagents led to the recovery of the unaltered starting material after several days under reaction conditions. The reaction with BnBr afforded the corresponding ketene dithioacetal mono-*S*-oxide **32**, resulting from dehydration.

Therefore we decided to first reduce the sulfinyl moiety of diastereoisomers **2**–**5** with $LiAlH_4$, which gave dithioacetal **6** as the major reaction product (THF reflux) or α-hydroxydithioacetals **7** and **8** (Et_2O reflux or THF at 45°C) depending on the reaction conditions used.[19] α-Hydroxydithioacetal **7**, with the *threo* configuration, has been protected as its corresponding *O*-acetyl, *O*-tetrahydropyranyl, and *O*-*t*-butyldimethylsilyl derivative (compounds **9**, **10** and **11**, see Table 1). So far as its epimer **8**, with the *erythro* configuration, is concerned, it has been treated under the same conditions leading to acetylation and formation of THP, TBDMS and benzyl ethers (compounds **12**–**15**, respectively, see Table 1). The protection reactions took place, in all the cases that we investigated, with excellent chemical yields (quantitative for THP and TBDMS derivatives). All these results demonstrate that this procedure enables the preparation of aldose derivatives bearing differently protected hydroxyl groups, which should be required for further stereoselective synthetic transformations.

Following our research project, we carried out the hydrolysis of the dithioacetal moiety in order to recover the free aldehyde, and through a second chain enlongation, attain five-carbon monosaccharides. Hydrolysis reactions of diethyldithioacetals **6**, **11**, **14** and **15** with HgO–$HgCl_2$ in acetone, gave rise to



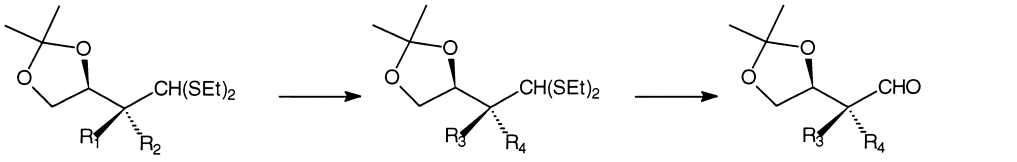
Scheme 1.

the corresponding aldehydes (**19**, **16**, **17** and **18**, respectively, see Table 1), in almost quantitative yields in all the cases considered.

As the starting materials to perform the chain elongation, we chose the *O*-silyl derivatives **16** and **17**, since they have a bulky protecting group, and therefore, the diastereoselectivity of the hydroxylation reaction should be presumably higher. We also used the 2-deoxy derivative **19**, aiming at the synthesis of the corresponding 3-deoxypentoses. Subsequent reaction of the aldehyde **17**, exhibiting D-*erythro* configuration, with the lithium salt of EETMS yielded a mixture of diastereoisomeric alcohols, which without further purification, was treated with the reducing agent $LiAlH_4$ to obtain the corresponding diethyldithioacetals with D-*ribo* **20** and D-arabino **21** configurations, in 88:12 ratio. The major stereoisomer **20** could be easily isolated.

In the reduction of the sulfinyl group, we observed concomitant desilylation. Hence, the next step involved the protection of hydroxyl groups with DMP under acidic conditions to reach the corresponding di-*O*-isopropylidene derivatives **22** and **23** (Scheme 2). We have chosen this protecting group because the di-*O*-isopropylidene derivative **22** is the precursor of its epimer **23**, produced through isomerization under basic conditions (following the procedure reported by Sharpless et al.[8]). The absolute configuration

Table 1
Reactions of protection of the hydroxyl group and hydrolysis of the dithioacetal



6: R_1=R_2=H
7: R_1=OH; R_2=H
8: R_1=H; R_2=OH

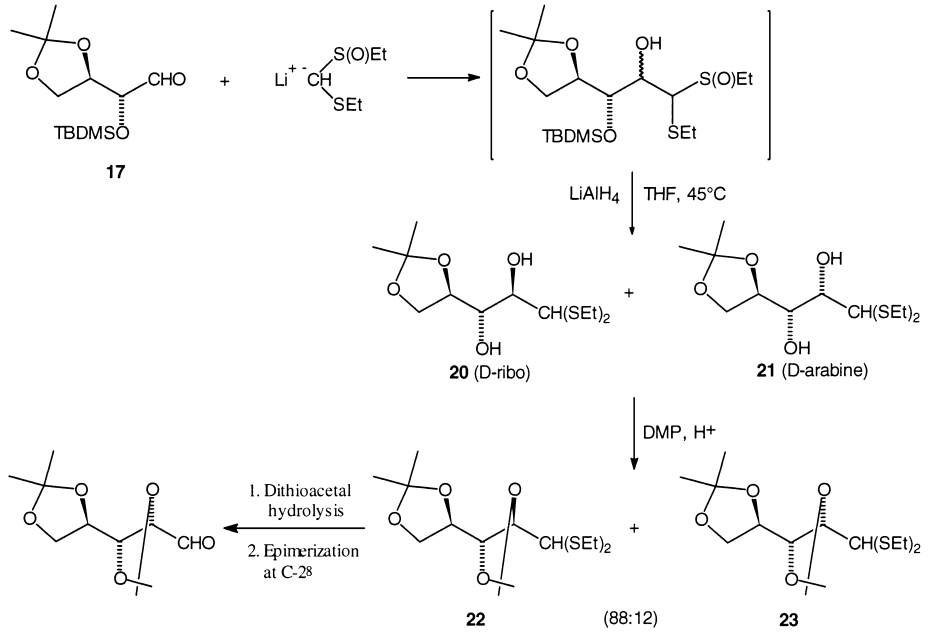
9-11: R_4=H
12-15: R_3=H

16: R_3=OTBDMS; R_4=H
17: R_3=H; R_4=OTBDMS
18: R_3=H; R_4=OBn
19: R_3=R_4=H

Substrate	R_3 (or R_4)	Product	Yield (%)[a]	Aldehyde (Yield)
7	$OCOCH_3$[b]	**9**[18b]	85	---
7	OTHP[c]	**10**	98	---
7	OTBDMS[d]	**11**	98	**16** (98%)
8	$OCOCH_3$[b]	**12**[18b]	90	---
8	OTHP[c]	**13**	98	---
8	OTBDMS[d]	**14**	98	**17** (98%)
8	OBn[e]	**15**	70	**18** (95%)
6	-	-	-	**19** (90%)

a: Isolated yield; b: Ac_2O/pyridine; c: 3,4-dihydro-2*H*-pyran/PTSA; d:TBDMSCl/DMF/Imidazole; e: BnBr/NaH/$^tBu_4NI$.

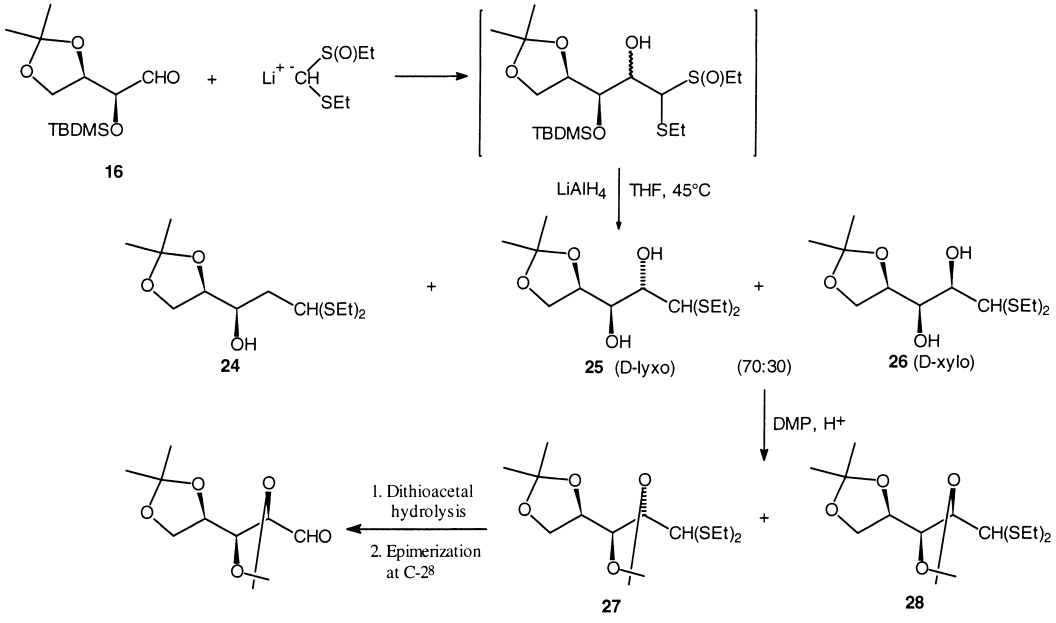
of epimers **22** and **23**, and therefore, that of compounds **20** and **21**, was elucidated by comparison with the products synthesized from natural D-ribose and D-arabinose following literature procedures.[20] ^1H and ^{13}C NMR spectra of these compounds were superimposable, and their specific rotations were similar in sign and magnitude.



Scheme 2.

So far as it is concerned with the chain elongation of the D-*threo* configured aldehyde **16**, the procedure

follows the same reaction sequence as described for compound **17**. In this case the reduction of the sulfinyl group led to diethyldithioacetals showing D-*lyxo* **25** and D-*xylo* **26** configurations, in a 70:30 ratio, as well as trace amounts of the corresponding 2-deoxyderivative **24** (Scheme 3). In this case, the diastereoselectivity of the process is only moderate, nevertheless both epimers can be easily separated and purified. The configuration of epimers **25** and **26** has been estabilised by their transformation into the corresponding di-*O*-isopropylidene derivatives, **27** and **28**, and their comparison with the products synthesized starting from the natural sugars, D-lyxose and D-xylose, respectively.[20] Their ^{1}H and ^{13}C NMR spectra were superimposable, and their specific rotations were similar in sign and magnitude. As in the previous case the di-*O*-isopropylidene derivative **25**, can be transformed into the corresponding aldose with D-*xylo* configuration.[8]



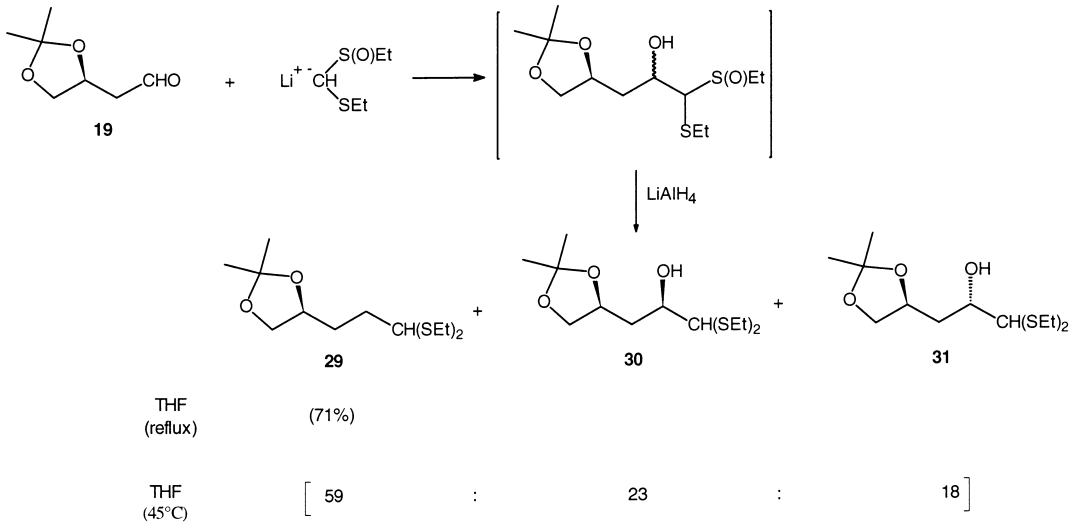
Scheme 3.

The usefulness of the di-*O*-isopropylidene derivatives **22** (D-*ribo*) and **27** (D-*lyxo*), obtained as the major products from the addition of EETMS to the aldehydes **17** (D-*erythro*) and **16** (D-*threo*), respectively, is even greater if we bear in mind that these compounds are precursors of the corresponding 2-deoxypentoses following the method described by Gray et al.[21]

Accordingly, in order to synthesize 3-deoxypentoses, we carried out the chain elongation of aldehyde **19**, with the lithium salt of EETMS and further reduction of the crude with $LiAlH_4$ in THF at 45°C. After this two-step sequence, the corresponding 3-deoxypentoses **30** and **31** were isolated only in small amounts, and, surprisingly, 2,3-dideoxypentose **29** was obtained as the major product. In another experiment carried out in refluxing THF, the compound **29** was obtained as the only product (Scheme 4). This result is a new 2,3-dideoxy-D-pentose[22] synthesis, which is a useful intermediate for the preparation of dideoxycytidine.[23]

^{1}H NMR data of the obtained diethyldithioacetal tetrose and pentose derivatives allowed us to establish a correlation between vicinal coupling constants (J_{vic}) and relative configuration (*erythro* or *threo*) for each compound. This correlation between configuration and conformation in diethyldithioacetals of alditols has been previously used to predict the most favored conformations so as to assign configurations.[24]

We observed that, in D-tetrose derivatives, the $J_{2,3}$ value is larger for compounds exhibiting *erythro*



Scheme 4.

Table 2
Vicinal coupling constants (Hz) of diethyldithioacetal of D-tetrose and D-pentose derivatives

comp.	$J_{3,4}$	$J_{2,3}$	$J_{2,3}$	$J_{3,4}$	comp.
7		3.7 *threo*	7.6 *erythro*		**8**
9		4.2 *threo*	7.0 *erythro*		**12**
10		3.5 *threo*	8.3 *erythro*		**13**
			7.0 *erythro*		**15**
25 *D-lyxo*	3.2 *threo*	8.5 *erythro*	7.1 *erythro*	8.2 *erythro*	**20** *D-ribo*
26 *D-xylo*	5.1 *threo*	1.5 *threo*	-	-	**21** *D-arabine*
27 *D-lyxo*	3.0 *threo*	5.7 *erythro*	6.5 *erythro*	9.3 *erythro*	**22** *D-ribo*
28 *D-xylo*	3.2 *threo*	7.4 *threo*	6.9 *threo*	7.3 *erythro*	**23** *D-arabine*

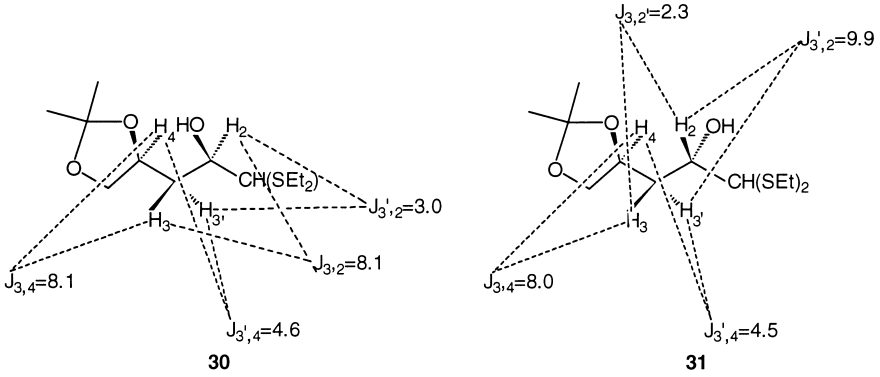
configuration (≥7 Hz for compounds **8**, **12**, **13** and **15**, see Table 2) than for compounds with *threo* configuration (≤4.2 Hz for compounds **7**, **9** and **10**).

In the case of D-pentose derivatives, we observed that compounds bearing hydrogens H-C3/H-C4 with *erythro* configuration show larger values of $J_{3,4}$ (≥7.3 Hz for compounds **20**, **22** and **23**) than those of their isomers bearing such hydrogens with *threo* configuration (≤5.1 Hz for compounds **25**–**28**). Concerning the values of $J_{2,3}$, this correlation can be established only for hydroxy derivatives, where the values of $J_{2,3}$ are larger for an *erythro* configuration (≥7.1 Hz for compounds **20** and **25**) than for a *threo* configuration (≤1.5 Hz for compound **26**, see Table 2).

Bearing in mind the dependence existing between the J_{vic} value and the dihedral angle formed by the implied hydrogen atoms, a preferential *syn* or *anti* arrangement of such hydrogens may be inferred, which would be related to a relative *threo* or *erythro* configuration, respectively. The observed deviation from the J_{vic} values of some of these derivatives may be due to the presence of bulky substituents (**11** and **14**,

see experimental section) or to the restrictions in the free bond rotation as a consequence of being part of a cycle ($J_{2,3}$ for compounds **22**, **23**, **27** and **28**).

A similar correlation was observed in the case of deoxy derivatives **6**, **30** and **31**, where a *syn* or *anti* relationship can also be inferred between vicinal hydrogens from the values of the coupling constants between such hydrogens. As shown in Scheme 5, isomer **30** has a J_{vic}=8.1 Hz at H-3, so a preferential *anti* arrangement of its vicinal hydrogens may be inferred. On the other hand, the geminal protons have a J≤4.6 Hz, which would be correct for a preferential *syn* disposition. From all these data we have assigned the *R** absolute configuration at C-2 for this compound. In contrast, isomer **31** possesses one $J_{vic}\geq 8$ Hz and another $J_{vic}\leq 4.5$ Hz at both hydrogens (3 and 3′), in accordance with an *anti* and *syn* geometry in relation to their vicinal hydrogens, which would be suitable for an *S** absolute configuration at C-2.



Scheme 5.

In summary, D-erythrose **8**, and D-threose **7**, α-hydroxydithioacetal derivatives (derived from 2,3-*O*-isopropylidene-D-glyceraldehyde **1** and EETMS) are stable intermediates which can be differently protected and easily converted into aldehydes with the aim of using them in subsequent synthetic transformations. Hydroxyalkylation of D-erythrose and D-threose derivatives, **16** and **17**, resulted in the total transformation of the starting product, so that the four stereoisomer D-pentoses can be obtained by this procedure. The same reaction sequence carried out on 2-deoxy-D-glycero tetrose gave rise to a 2,3-dideoxy-D-glycero pentose derivative **29**, in high yield. Additionally, the vicinal coupling constant values of the obtained diethyldithioacetals D-tetrose and D-pentose derivatives, enable the assignment of an *anti* or a *syn* relationship between vicinal hydrogens, which is related to their relative *erythro* or *threo* configuration, respectively.

3. Experimental

3.1. General methods

Dry solvents and liquid reagents were distilled under argon just prior to use: THF and diethyl ether were distilled from sodium and benzophenone ketyl; EETMS was distilled at reduced pressure. NaH (60% mineral oil) was activated by repeated treatment with hexane, and further removing the solvent at reduced pressure. All reactions vessels, after being flame-dried, were kept under argon. Organic solutions were dried over anhydrous sodium or magnesium sulfate, and the solvent was evaporated at reduced pressure below 40°C.

TLC was performed on glass plates coated with silica gel G (Merck) or SI-F-254 (Scharlau), spots being developed either with sulfuric acid in ethanol (10%) or with phosphomolybdic acid in ethanol.

Column chromatographic separations were determined by using silica gel Merck 60 (70–230 mesh, ASTM, for gravity chromatography) or 230–400 mesh (for flash chromatography).

Optical rotations were measured with a 141 Perkin–Elmer polarimeter. Specific rotations are given in units of 10^{-1} deg cm^2 g^{-1}.

^{1}H NMR spectra (300 MHz, $CDCl_3$) and ^{13}C NMR (80 MHz, $CDCl_3$) were determined with a Bruker AC-300 spectrometer. Chemical shifts were measured in ppm (δ), relative to $SiMe_4$ as the internal reference; signal multiplicities are quoted as s, singlet; d, doublet; dd, double doublet; ddd, doubled double doublet; dddd, double double doublet; dq, double quartet; t, triplet; q, quartet, and m, multiplet. J values are given in hertz. Diastereoisomeric ratios were determined by integration of well separated signals of ^{1}H NMR spectra. IR spectra were measured using a Nicolet FTIR-20-SX spectrometer. Mass spectra were recorded by the direct insertion technique by electronic impact (EI), using an HP-588-A spectrometer at 230 eV with a source temperature of 200°C. Elemental analyses were determined with a Carlo Erba elemental analyzer 1106.

2,3-*O*-Isopropylidene-D-glyceraldehyde **1**, was synthesized from 1,2:5,6-di-*O*-isopropylidene-D-mannitol by oxidation with sodium periodate.[5b] 2-Deoxi-3,4-*O*-isopropylidene-D-glycero-tetrose **6**, 3,4-*O*-isopropylidene-D-threose **7**, 3,4-*O*-isopropylidene-D-erythrose-**8** diethyldithioacetals,[19] and their *O*-acetyl derivatives[18b] **9** and **12**, were prepared as previously described.

*3.2. General method for protection with 3,4-dihydro-2*H*-pyran*[25]

*3.2.1. Of alcohol **7***

To a solution of compound **7** (250 mg, 0.94 mmol) and 3,4-dihydro-2*H*-pyran (395 mg, 4.7 mmol), in CH_2Cl_2 (4 ml), at 20°C, PTSA (9 mg, 10^{-3} mmol) was added. The mixture was stirred for 2 h at the same temperature, poured into Et_2O (6 ml) and washed with saturated aqueous solution of $NaHCO_3$ (6 ml), and NaCl (6 ml), and extracted with ether (3×6 ml). The combined ethereal layers were dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (hexane:Et_2O, 25:1) to give compound **10** (320 mg, 0.92 mmol, 98%) as a colorless oil.

*3.2.1.1. 2-*O*-Tetrahydropyranyl-3,4-*O*-isopropylidene-*D*-threose diethyldithioacetal **10**.* R_f=0.52 (hexane:Et_2O, 2:1); $[\alpha]_D^{20}$=+19.1 (c 0.1, $CHCl_3$); ^{1}H NMR δ 1.19–1.48 (m, 12H, ($CH_3CH_2S)_2$- and $C(CH_3)_2$), 1.50–1.65 (m, 4H, H–C4′ and H–C5′), 1.68–1.91 (m, 2H, H–C6′), 2.71–2.78 (m, 4H, ($CH_3CH_2S)_2$-), 3.45–3.92 (m, 2H, H–C3′), 4.04 (dd, 1H, $J_{3,4}$ 6.9, J_{gem} 8.2, H–C4), 4.10 (d, 1H, $J_{1,2}$ 3.0, H–C1), 4.11 (dd, 1H, $J_{3,4'}$ 6.6, J_{gem} 8.2, H′–C4), 4.25 (dd, 1H, $J_{2,1}$ 3.0, $J_{2,3}$ 3.5, H–C2), 4.42 (ddd, 1H, $J_{3,2}$ 3.5, $J_{3,4}$ 6.9, $J_{3,4'}$ 6.6, H–C3), 4.83 (dd, 1H, $J_{1',6'a}$ 2.8, $J_{1',6'b}$ 4.8, H–C1′); ^{13}C NMR δ 14.1 and 14.5 (($CH_3CH_2S)_2$-), 19.8, 25.1, 25.4, 26.2, 30.7 (($CH_3CH_2S)_2$-, C-4′, C-5′, C-6′), 25.1 and 26.6 ($C(CH_3)_2$), 53.0 (C-1), 62.9 and 65.3 (C-3′, C-4), 76.6 and 80.8 (C-2, C-3), 100.7 (C-1′), 107.9 ($C(CH_3)_2$); IR (KBr, liquid film): 3000, 1455, 1385, 1375, 1260, 1210, 1160, 1130, 1060, 975, 870, 815 cm^{-1}; MS (m/e) (relative intensity): 350 (0.2, M^+), 335 (0.3, M^+-CH_3), 289 (0.2, $M^+-C_2H_5S$), 248 (4, $C_{11}H_{20}O_2S_2^+$), 135 (40, $C_5H_{11}S_2^+$), 101 (33, $C_5H_9O_2^+$), 85 (100, $C_5H_9O^+$), 43 (26, $C_2H_3O^+$). Anal. calcd for $C_{16}H_{30}O_4S_2$: C, 54.82; H, 8.63. Found: C, 54.75; H, 8.60.

*3.2.2. Of alcohol **8***

Following the same above-described procedure, starting from compound **8** (240 mg, 0.9 mmol) in CH_2Cl_2 (4 ml), 3,4-dihydro-2*H*-pyran (379 mg, 4.5 mmol) and PTSA (1.72 mg, 9.05×10^{-3} mmol), compound **13** (310 mg, 0.88 mmol, 98%) was obtained as a colorless oil after column chromatography (hexane:Et_2O, 20:1).

*3.2.2.1. 2-*O*-Tetrahydropyranyl-3,4-*O*-isopropylidene-*D*-erythrose diethyldithioacetal* ***13***. R_f=0.64 (hexane:Et_2O, 2:1); $[\alpha]_D^{20}$=+77.9 (c 0.52, $CHCl_3$); ^{1}H NMR δ 1.27 and 1.29 (2t, each 3H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.35 and 1.41 (2s, each 3H, $C(CH_3)_2$), 1.52–1.80 (m, 6H, H-C4′, H-C5′, and H-C6′), 2.67 and 2.74 (2c, each 2H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 3.46–3.93 (m, 2H, H-C3′), 3.98 (dd, 1H, $J_{2,1}$ 1.5, $J_{2,3}$ 8.3, H–C2), 4.10 (dd, 1H, $J_{4,3}$ 6.3, J_{gem} 8.6, H–C4), 4.15 (d, 1H, $J_{1,2}$ 1.5, H–C1), 4.20 (dd, 1H, $J_{4',3}$ 5.0, J_{gem} 8.6, H–C4), 4.34 (ddd, 1H, $J_{3,2}$ 8.3, $J_{3,4}$ 6.3, $J_{3,4'}$ 5.0, H–C3), 4.95–4.97 (m, 1H, H–C1′); ^{13}C NMR δ 14.5 and 14.6 (($CH_3CH_2S)_2$-), 20.2, 25.2, 25.4, 26.3, 30.7 (($CH_3CH_2S)_2$-, C-4′, C-5′, C-6′), 25.2 and 26.9 ($C(CH_3)_2$), 53.3 (C-1), 63.7 and (C-3′, C-4), 75.2 and 81.5 (C-2, C-3), 100.6 (C-1′), 109.2 ($C(CH_3)_2$); IR (KBr, liquid film): 3000, 1455, 1385, 1375, 1260, 1220, 1160, 1130, 975, 855, 790 cm^{-1}; MS (m/e) (relative intensity): 350 (1%, M^+), 289 (0.5, $M^+-C_2H_5S$), 248 (5, $C_{11}H_{20}O_2S_2^+$), 220 (14, $C_9H_{16}O_2S_2^+$), 135 (55, $C_5H_{11}S_2^+$), 101 (32, $C_5H_9O_2^+$), 85 (100, $C_5H_9O^+$), 43 (19, $C_2H_3O^+$). Anal. calcd for $C_{16}H_{30}O_4S_2$: C, 54.82; H, 8.63. Found: C, 54.75; H, 8.60.

3.3. General method for O*-silylation*[15c]

3.3.1. Of alcohol ***7***

To a solution of compound **7** (798 mg, 3 mmol) in DMF (2 ml), imidazole (408 mg, 6 mmol) and *t*-$BuMe_2SiCl$ (1.3 g, 6 mmol) were added. The solution was stirred at 70°C for 50 h, cooled to rt, poured into water (100 ml), and extracted with Et_2O (2×45 ml). The combined ethereal layers were dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (hexane:Et_2O, 20:1) to give compound **11** (1.12 g, 2.94 mmol, 98%) as a colorless oil.

*3.3.1.1. 2-*O*-(*t*-Butyldimethylsilyl)-3,4-*O*-isopropylidene-*D*-threose diethyldithioacetal* ***11***. R_f=0.81 (hexane:Et_2O, 2:1); $[\alpha]_D^{20}$=−29.3 (c 0.52, $CHCl_3$); ^{1}H NMR δ 0.12 and 0.15 (2s, each 3H, $(CH_3)_2Si$-), 0.92 (s, 9H, $(CH_3)_3CSi$-), 1.25 and 1.26 (2t, each 3H, J_{vic} 7.4, J_{vic} 7.5, ($CH_3CH_2S)_2$-), 1.35 and 1.40 (2s, each 3H, $C(CH_3)_2$), 2.63 and 2.78 (2c, each 2H, J_{vic} 7.5, ($CH_3CH_2S)_2$-), 3.66 (d, 1H, $J_{1,2}$ 2.2, H–C1), 3.71 (dd, 1H, $J_{4,3}$=J_{gem} 8.0, H–C4), 3.99 (dd, 1H, $J_{2,1}$ 2.2, $J_{2,3}$ 7.2, H–C2), 4.05 (dd, 1H, $J_{4',3}$ 6.2, J_{gem} 8.0, H′–C4), 4.29–4.36 (m, 1H, H-3); ^{13}C NMR δ −4.1 and −4.7 ($(CH_3)_2Si$-), 14.5 (($CH_3CH_2S)_2$-), 18.5 ($(CH_3)_3CSi$-), 24.9 and 26.1 (($CH_3CH_2S)_2$-), 25.5 and 26.6 ($C(CH_3)_2$), 26.0 ($(CH_3)_3CSi$-), 26.1 (CH_3CH_2S-), 26.6 ($C(CH_3)_2$), 54.4 (C-1), 65.8 (C-4), 78.5 and 78.8 (C-2 and C-3), 108.9 ($C(CH_3)_2$); IR (KBr, liquid film): 2995, 1470, 1460, 1385, 1375, 1260, 1220, 1130, 1075, 840, 780 cm^{-1}; MS (m/e) (relative intensity): 380 (0.2%, M^+), 365 (2, M^+-Me), 323 (10, M^+-t-Bu), 305 (4, $C_{14}H_{29}O_3SSi^+$), 265 (50, $C_{11}H_{21}O_3S_2^+$), 161 (26, $C_6H_9O_3S^+$), 135 (38, $C_5H_{11}S_2^+$), 101 (100, $C_5H_9O_2^+$), 73 (84, $C_3H_5O_2^+$), 59 (29, $C_3H_7O^+$), 43 (49, $C_2H_3O^+$). Anal. calcd for $C_{17}H_{36}O_3S_2Si$: C, 53.64; H, 9.53. Found: C, 53.68; H, 8.95.

3.3.2. Of alcohol ***8***

Following the above-described procedure for the silylation of compound **7**, starting from compound **8** (1.46 g, 5.49 mmol) in DMF (4 ml), imidazole (747 mg, 10.98 mmol) and *t*-$BuMe_2SiCl$ (1.7 g, 11.35 mmol), compound **14** (2.05 g, 5.40 mmol, 98% yield) was obtained as a colorless oil after chromatographic purification (hexane:Et_2O, 20:1).

*3.3.2.1. 2-*O*-(*t*-Butyldimethylsilyl)-3,4-*O*-isopropylidene-*D*-erythrose diethyldithioacetal* ***14***. R_f=0.78 (hexane:Et_2O, 2:1); $[\alpha]_D^{20}$=+17.2 (c 0.52, $CHCl_3$); ^{1}H NMR δ 0.12 and 0.20 (2s, each 3H, $(CH_3)_2Si$-), 0.89 (s, 9H, $(CH_3)_3CSi$-), 1.27 (t, 6H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.33 and 1.40 (2s, each 3H, $C(CH_3)_2$),

2.60–2.77 (m, 4H, $(CH_3CH_2)_2S$-), 3.90 (dd, 1H, $J_{4,3}$ 6.1, J_{gem} 8.3, H–C4), 3.99 (d, 1H, $J_{1,2}$ 1.8, H–C1), 4.01 (dd, 1H, $J_{2,1}$ 1.8, $J_{2,3}$ 6.1, H–C2), 4.08 (dd, 1H, $J_{4',3}$ 6.4, J_{gem} 8.3, H′–C4), 4.30 (ddd, 1H, $J_{3,2}=J_{3,4}$ 6.1, $J_{3,4'}$ 6.4, H–C3); ^{13}C NMR δ −3.6 and −4.5 ($(CH_3)_2Si$-), 14.5 and 14.6 ($(CH_3CH_2S)_2$-), 18.3 ($(CH_3)_3CSi$-), 25.0 and 26.6 ($C(CH_3)_2$), 25.8 and 26.6 ($(CH_3CH_2S)_2$), 25.9 ($(CH_3)_3CSi$-), 54.7 (C-1), 66.6 (C-4), 76.5 and 77.2 (C-2, C-3), 108.6 ($C(CH_3)_2$); IR (KBr, liquid film): 2995, 1475, 1465, 1385, 1375, 1260, 1220, 1130, 1075, 835, 780 cm^{-1}; MS (m/e) (relative intensity): 380 (0.2%, M^+), 365 (0.6, M^+−Me), 323 (6, M^+−*t*-Bu), 305 (1, $C_{14}H_{29}O_3SSi^+$), 265 (8, $C_{11}H_{21}O_3S_2^+$), 161 (34, $C_6H_9O_3S^+$), 135 (45, $C_5H_{11}S_2^+$), 101 (100, $C_5H_9O_2^+$), 73 (63, $C_3H_5O_2^+$), 59 (20, $C_3H_7O^+$), 43 (35, $C_2H_3O^+$). Anal. calcd for $C_{17}H_{36}O_3S_2Si$: C, 53.64; H, 9.53. Found: C, 53.68; H, 8.95.

3.4. General method for O-*benzylation*[15c]

3.4.1. Of alcohol ***8***

To a solution of compound **8** (1.34 g, 5.04 mmol) in THF (60 ml), a 60% suspension of NaH (129 mg, 5.36 mmol) in mineral oil was added at rt. The mixture was stirred at reflux for 30 min, cooled at rt and then *t*-Bu_4NI (157 mg, 0.43 mmol) and benzylbromide (0.64 ml, 5.36 mmol) were successively added. The solution was stirred for 2 h at rt, the solvent was removed in vacuo and the residue was treated with a saturated aqueous solution of $NaHCO_3$ (50 ml) and extracted with CH_2Cl_2 (2×30 ml). The combined organic extracts were dried (Na_2SO_4), the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane:Et_2O, 4:1) to yield compound **15** (1.26 g, 3.53 mmol, 70%) as a colorless oil.

*3.4.1.1. 2-*O*-Benzyl-3,4-*O*-isopropylidene-*D*-erythrose diethyldithioacetal* ***15***. R_f=0.64 (hexane:Et_2O, 1:1); $[\alpha]_D^{20}$=+39.6 (c 1.06, $CHCl_3$); ^{1}H NMR δ 1.25 and 1.29 (2t, each 3H, J_{vic} 7.4, $(CH_3CH_2S)_2$-), 1.34 and 1.40 (2s, each 3H, $C(CH_3)_2$), 2.66–2.76 (m, 4H, $(CH_3CH_2S)_2$-), 3.86 (dd, 1H, $J_{2,1}$ 2.3, $J_{2,3}$ 6.8, H–C2), 3.89 (dd, 1H, $J_{4,3}$ 5.7, J_{gem} 8.6, H–C4), 4.08 (dd, 1H, $J_{4',3}$ 6.4, J_{gem} 8.6, H′–C4), 4.09 (d, 1H, $J_{1,2}$ 2.3, H–C1), 4.37 (ddd, 1H, $J_{3,2}$ 6.8, $J_{3,4}$ 5.7, $J_{3,4'}$ 6.4, H–C3), 4.72 and 4.92 (AB system, 2H, J 11.3, $PhCH_2$-), 7.26–7.38 (m, 5H, C_6H_5-); ^{13}C NMR δ 14.4 and 14.5 ($(CH_3CH_2S)_2$-), 25.1 and 26.7 ($C(CH_3)_2$), 25.5 and 26.3 ($(CH_3CH_2S)_2$-), 53.2 (C-1), 66.5 (C-4), 74.7 ($PhCH_2$), 75.9 and 83.0 (C-2, C-3), 108.8 ($C(CH_3)_2$), 127.7, 127.9 and 128.2 (C_6H_5), 137.93 (C_{Ph}–CH_2); IR (KBr, liquid film): 3050, 3000, 1460, 1385, 1375, 1270, 1220, 1170, 1060, 855, 750 cm^{-1}; MS (m/e) (relative intensity): 356 (2%, M^+), 295 (2, M^+−C_2H_5S), 248 (3, $C_{11}H_{20}O_2S_2^+$), 188 (4, $C_9H_{16}O_2S^+$), 135 (84, $C_5H_{11}S_2^+$), 101 (30, $C_5H_9O_2^+$), 91 (100, $C_7H_7^+$), 43 (53, $C_2H_30^+$). Anal. calcd for $C_{18}H_{28}O_3S_2$: C, 60.63; H, 7.92. Found: C, 60.75; H, 7.93.

3.4.2. Of alcohols ***2*** *and* ***3***

Following the above-described procedure for the benzylation of compound **8**, starting from the diastereoisomeric alcohols[26] **2** and **3** (1.13 g, 4 mmol) in THF (50 ml), NaH (170 mg, 4.25 mmol), *t*-BuNI (148 mg, 0.4 mmol) and benzylbromide (0.5 ml, 4.25 mmol), **32** (726 mg, 2.8 mmol, 70%, reaction time 4 h) was isolated as a colorless oil by flash chromatography (hexane:Et_2O, 1:1).

*3.4.2.1. (1*S*)-1-Ethylsulfinyl-1-ethylthio-2-deoxy-3,4-*O*-isopropylidene-*D*-glycero-tetra-1-enose* ***32***. R_f=0.55 (Et_2O); $[\alpha]_D^{20}$=+127.4 (c 0.5, $CHCl_3$); ^{1}H NMR δ 1.19 (t, 3H, J_{vic} 7.3, CH_3CH_2S-), 1.30 (t, 3H, J_{vic} 7.3, CH_3CH_2SO), 1.42 and 1.45 (2s, each 3H, $C(CH_3)_2$), 2.67–3.20 (m, 4H, CH_3CH_2S-, CH_3CH_2SO-), 3.64 (dd, 1H, $J_{4,3}$ 6.9, J_{gem} 8.2, H–C4), 4.18 (dd, 1H, $J_{4',3}$ 6.9, J_{gem} 8.2, H′–C4), 5.24

(ddd, 1H, $J_{3,2}$ 8.2, $J_{3,4}$=$J_{3,4'}$ 6.9, H–C3), 6.90 (d, 1H, $J_{2,3}$ 8.2, H–C2); ^{13}C NMR δ 14.8 and 15.0 (CH_3CH_2S, CH_3CH_2SO), 25.8 and 26.5 ($C(CH_3)_2$), 29.6 (CH_3CH_2S-), 44.7 (CH_3CH_2SO), 68.9 (C-4), 73.3 (C-3), 110.2 ($C(CH_3)_2$), 139.8 (C-1), 141.2 (C-2); IR (KBr, liquid film): 3000, 1610, 1460, 1385, 1375, 1250, 1220, 1160, 1065, 970, 840, 760 cm^{-1}; MS (m/e) (relative intensity): 264 (1%, M^+), 239 (3, M^+−Me), 189 (2, $C_9H_{17}O_2S^+$), 161 (12, $C_6H_9OS_2^+$), 145 (3, $C_6H_9S_2^+$), 101 (37, $C_5H_9O_2^+$), 59 (34, $C_3H_7O^+$), 43 (100, $C_2H_3O^+$). Anal. calcd for $C_{11}H_{20}O_3S_2$: C, 49.98; H, 7.62. Found: C, 50.03; H, 7.59.

3.5. *General method for dithioacetals hydrolysis*[18a]

3.5.1. *Of dithioacetal* ***11***

Compound **11** (740 mg, 1.95 mmol) in a mixture of acetone (6 ml) and water (0.5 ml) was treated with $HgCl_2$ (1.25 g, 4.6 mmol) and HgO (1.25 g, 5.78 mmol). The reaction mixture was stirred for 2 h at rt. The solvent was removed in vacuo, $CHCl_3$ was added and then the mixture was filtered through a Celite pad and washed with the same solvent. The filtrate was treated with saturated aqueous solution of KI and water. The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give pure **16** (535 mg, quantitative yield) as a colorless oil.

*3.5.1.1. 2-*O*-(*t*-Butyldimethylsilyl)-3,4-*O*-isopropylidene-*D*-threose* ***16***. R_f=0.57 (hexane:Et_2O, 2:1); $[\alpha]_D^{20}$=+182.3 (c 0.85, $CHCl_3$); spectroscopic data for compound **16** are coincident with those reported:[15c] ^{1}H NMR δ 0.08 and 0.10 (2s, each 3H, $(CH_3)_2Si$-), 0.92 (s, 9H, $(CH_3)_3CSi$-), 1.33 and 1.41 (2s, each 3H, $C(CH_3)_2$), 3.93 (dd, 1H, $J_{4,3}$ 6.1, J_{gem} 8.8, H–C4), 4.04 (dd, 1H, $J_{2,1}$ 1.3, $J_{2,3}$ 4.9, H–C2), 4.06 (dd, 1H, $J_{4',3}$ 6.6, J_{gem} 8.8, H′–C4), 4.30 (ddd, 1H, $J_{3,2}$ 4.9, $J_{3,4}$ 6.1, $J_{3,4'}$ 6.6, H–C3), 9.68 (d, 1H, $J_{1,2}$ 1.3, H–C1).

3.5.2. *Of dithioacetal* ***14***

Following the above-described hydrolysis procedure, starting from compound **14** (1.98 g, 5.21 mmol) in acetone–water (16 ml), $HgCl_2$ (3.34 g, 12.3 mmol) and HgO (3.34 g, 15.4 mmol), pure **17** (1.5 g, quantitative yield) was obtained as a colorless oil.

*3.5.2.1. 2-O-(*t*-Butyldimethylsilyl)-3,4-O-isopropylidene-*D*-erythrose* ***17***. R_f=0.6 (hexane:Et_2O, 2:1); $[\alpha]_D^{20}$=−1.2 (c 1.0, $CHCl_3$); spectroscopic data of **17** are coincident with those reported:[15c] ^{1}H NMR δ 0.08 and 0.10 (2s, each 3H, $(CH_3)_2Si$-), 0.91 (s, 9H, $(CH_3)_3CSi$-), 1.34 and 1.43 (2s, each 3H, $C(CH_3)_2$), 3.92 (dd, 1H, $J_{4,3}$ 5.9, J_{gem} 8.4, H–C4), 4.02 (dd, 1H, $J_{4',3}$ 6.1, J_{gem} 8.4, H′–C4), 4.05 (dd, 1H, $J_{2,1}$ 1.6, $J_{2,3}$ 6.1, H–C2), 4.24 (m, 1H, H–C3), 9.65 (1H, d, $J_{1,2}$ 1.6, H–C1).

3.5.3. *Of dithioacetal* ***15***

Following the above-described hydrolysis procedure, starting from compound **15** (1.98 g, 5.21 mmol) in acetone–water (16 ml), $HgCl_2$ (3.34 g, 12.3 mmol) and HgO (3.34 g, 15.4 mmol), pure **18** (1.5 g, quantitative yield) was achieved as a colorless oil.

*3.5.3.1. 2-*O*-(Benzyl)-3,4-*O*-isopropylidene-*D*-erythrose* ***18***. R_f=0.4 (hexane:Et_2O, 1:2); $[\alpha]_D^{20}$=+28.7 (c 1.2, $CHCl_3$); spectroscopic data of compound **18** are coincident with those previously reported:[15c] ^{1}H NMR δ 1.34 and 1.43 (2s, each 3H, $C(CH_3)_2$), 3.82 (dd, 1H, $J_{1,2}$ 2.0, $J_{2,3}$ 6.1, H–C2), 3.92 (dd, 1H, $J_{4,3}$ 5.5, J_{gem} 8.6, H–C4), 4.07 (dd, 1H, $J_{4',3}$ 6.3, J_{gem} 8.6, H′–C4), 4.35 (ddd, 1H, $J_{3,4}$ 5.5, $J_{3,2}$ 6.1, $J_{3,4'}$ 6.3, H–C3), 4.73 (AB system, 2H, J_{gem} 11.6, $PhCH_2$-), 7.35 (d, 1H, $J_{1,2}$ 2.0, H–C1).

3.5.4. Of dithioacetal ***6***

Following the above-mentioned procedure for the hydrolysis of compound **11**, starting from compound **6** (355 mg, 1.42 mmol) in acetone–water (5 ml), $HgCl_2$ (908 mg, 3.34 mmol), and HgO (908 mg, 4.19 mmol), pure **19** (184 mg, 90%) was obtained as a colorless oil.

*3.5.4.1. 2-Deoxy-3,4-*O*-isopropylidene-*D*-glycero tetrose* ***19***. R_f=0.23 (hexane:isopropanol, 25:1); $[\alpha]_D^{20}$=+17.5 (c 0.6, $CHCl_3$); ^{1}H NMR δ 1.37 and 1.42 (2s, each 3H, $C(CH_3)_2$), 2.65 (ddd, 1H, $J_{2,1}$ 1.2, $J_{2,3}$ 6.1, J_{gem} 17.3, H–C2), 2.85 (ddd, 1H, $J_{2',1}$ 1.8, $J_{2',3}$ 6.7, J_{gem} 17.3, H′–C2), 3.59 (dd, 1H, $J_{4,3}$ 6.7, J_{gem} 8.3, H–C4), 4.19 (dd, 1H, $J_{4',3}$ 6.1, J_{gem} 8.3, H′–C4), 4.54 (dddd, 1H, $J_{3,2}$=$J_{3,4'}$ 6.1, $J_{3,2'}$=$J_{3,4}$ 6.7, H–C3), 9.81 (dd, 1H, $J_{1,2}$ 1.2, $J_{1,2'}$ 1.8, H–C1); ^{13}C NMR δ 25.5 and 26.8 ($C(CH_3)_2$), 47.8 (C-2), 69.1 (C-4), 70.6 (C-3), 109.3 ($C(CH_3)_2$), 200.1 (C-1); IR (KBr, liquid film): 3000, 2750, 1730, 1460, 1385, 1375, 1230, 1160, 1070 cm^{-1}; MS (m/e) (relative intensity): 129 (7%, M^+-CH_3), 116 (1, M^+-CO), 114 (1, $C_6H_{10}O_2^+$), 101 (3, $C_5H_9O_2^+$), 85 (7, $C_4H_5O_2^+$), 69 (100, $C_4H_5O^+$), 59 (17, $C_3H_7O^+$), 43 (3, $C_2H_3O^+$). Anal. calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.21; H, 8.43.

3.6. Addition of EETMS to aldehydes. General procedure[18]

3.6.1. To aldehyde ***17***

1.6 M *n*-BuLi (4 ml, 6.45 mmol) was added dropwise to a solution of EETMS (784 mg, 5.16 mmol) in dry THF (3 ml) at −20°C. The solution was warmed to 0°C and stirred for 30 min. Aldehyde **17** (1.4 g, 5.16 mmol) in THF (2 ml) was slowly added at −50°C and the reaction mixture was allowed to reach room temperature (for ca. 90 min), then quenched with saturated aqueous NH_4Cl solution and extracted with dichloromethane (2×3 ml) and ethyl acetate (3 ml). The combined organic extracts were dried (Na_2SO_4) and the solvent was removed in vacuo. The crude reaction (2.3 g; quantitative yield by ^{1}H NMR spectrum) was dissolved in THF (15 ml), and without further purification, treated with $LiAlH_4$ (600 mg, 15.8 mmol). The reaction mixture was warmed at 45°C and stirred for 4 h. The above-described work-up yielded a residue, which was purified by flash chromatography (hexane:Et_2O, 5:1) affording the product **20** (1.02 g, 3.44 mmol, 67% yield) and a mixture of **20** and **21** (237 mg, 0.8 mmol, 16% yield). Successive flash chromatography (hexane:Et_2O, 20:1) did not allow isolation of stereoisomer **21** as a pure form.

The diastereomeric ratio (88:12) was determined by integration of well separated signals (H–C5) of the ^{1}H NMR spectrum by further transformation of an aliquot of the reaction mixture into the corresponding di-*O*-isopropylidene derivatives, **22** and **23**.

*3.6.1.1. 4,5-*O*-Isopropylidene-*D*-ribose diethyldithioacetal* ***20***. R_f=0.30 (hexane:Et_2O, 1:1); $[\alpha]_D^{20}$=+9.4 (c 2.03, $CHCl_3$); ^{1}H NMR δ 1.29 (t, 6H, J_{vic} 7.4, $(CH_3CH_2S)_2$-), 1.37 and 1.45 (2s, each 3H, $C(CH_3)_2$), 2.66–2.78 (m, 5H, $(CH_3CH_2S)_2$-, HO–C3), 3.15 (d, 1H, $J_{OH,2}$ 3.6, HO–C2, exchangeable with D_2O), 3.75 (ddd, 1H, $J_{2,1}$ 4.1, $J_{2,OH}$ 3.6, $J_{2,3}$ 7.1, H–C2, the signal turned into dd on addition of D_2O, $J_{2,1}$ 4.1, $J_{2,3}$ 7.1), 3.98 (m, 1H, H–C3, the signal turned into dd on addition of D_2O, $J_{3,2}$ 7.1, $J_{3,4}$ 8.2), 4.05–4.11 (m, 2H, H–C4 and H–C5), 4.22 (d, 1H, $J_{1,2}$ 4.1, H–C1), 4.38 (dd, 1H, $J_{4,5'}$ 6.6, J_{gem} 11.8, H′–C5); ^{13}C NMR δ 14.4 and 14.7 ($(CH_3CH_2)_2$S-), 25.6 ($(CH_3CH_2S)_2$-), 26.4 ($C(CH_3)_2$), 54.5 (C-1), 65.30 (C-5), 71.1, 74.5 and 76.3 (C-2, C-3, C-4), 109.1 ($C(CH_3)_2$); IR (KBr, liquid film): 3475, 3000, 1455, 1385, 1375, 1215, 1160, 1065, 860, 790 cm^{-1}; MS (m/e) (relative intensity): 296 (2%, M^+), 235 (2, $M^+-C_2H_5S$), 217 (1, $C_{10}H_{17}O_3S^+$), 177 (15, $C_7H_{13}OS_2^+$), 161 (4, $C_7H_{13}O_4^+$), 135

(100, $C_5H_{11}S_2^+$), 75 (45, $C_3H_5S^+$), 59 (50, $C_3H_7O^+$), 43 (49, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_4S_2$: C, 48.62; H, 8.16. Found: C, 48.68; H, 8.14.

*3.6.1.2. 4,5-*O*-Isopropylidene-*D*-arabinose diethyldithioacetal **21**.* ^{1}H NMR δ 1.29 (t, 6H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.36 and 1.43 (2s, each 3H, $C(CH_3)_2$), 2.60–2.79 (m, 4H, ($CH_3CH_2S)_2$-), 3.39 (d, 1H, J_{vic} 2.3, HO), 3.74–3.76 (m, 1H, HO), 3.94–4.22 (6H, m, H–C1, H–C2, H–C3, H–C4, H–C5, H′–C5); ^{13}C NMR δ 14.4 and 14.5 (($CH_3CH_2S)_2$-), 23.5 and 25.2 (($CH_3CH_2S)_2$-), 25.4 and 26.9 ($C(CH_3)_2$), 55.6 (C-1), 67.1 (C-5), 70.2, 71.1 and 76.2 (C-2, C-3, C-4), 109.1 ($C(CH_3)_2$).

*3.6.2. To aldehyde **16***

Following the above-described procedure for the addition of EETMS to compound **17**, starting from compound **16** (534 mg, 1.95 mmol) in THF (1 ml), EETMS (296 mg, 1.95 mmol) and *n*-BuLi (1.52 ml, 2.44 mmol), 900 mg (quantitative yield by ^{1}H NMR spectrum) of crude reaction were obtained, and without further purification, dissolved in THF (5 ml) and treated at 45°C with $LiAlH_4$ (225 mg, 5.9 mmol). The work-up described above led to a crude product containing compounds **24**, **25** and **26** in a 9:64:27 ratio (estimated by integration of the signals corresponding to H–C5 in the ^{1}H NMR spectrum of the crude reaction). Column chromatography using hexane:Et_2O (10:1) as the eluent afforded pure **24** (27 mg, 5% yield) as a colorless oil and a fraction (387 mg, 67% yield) containing a mixture of compounds **25** and **26**. After subsequent flash chromatography (hexane:Et_2O, 15:1) pure **25** and **26** were obtained as colorless oils.

*3.6.2.1. 2-Deoxy-4,5-*O*-isopropylidene-*D*-*threo* pentose diethyldithioacetal **24**.* R_f=0.40 (hexane:Et_2O, 1:1), $[\alpha]_D^{20}$=27.5 (c 1.5, $CHCl_3$); ^{1}H NMR δ 1.27 (t, 6H, J_{vic} 7.5, ($CH_3CH_2S)_2$-), 1.37 and 1.45 (2s, each 3H, $C(CH_3)_2$), 1.74 (ddd, 1H, $J_{2,1}$ 10.3, J_{gem} 14.3, $J_{2,3}$ 2.6, H–C2), 2.04 (ddd, 1H, $J_{2',1}$ 4.3, J_{gem} 14.3, $J_{2',3}$ 9.9, H–C2), 2.35 (d, 1H, $J_{OH,3}$ 6.0, HO–C3, exchangeable with D_2O), 2.56–2.77 (m, 4H, ($CH_3CH_2S)_2$-), 3.75–3.82 (m, 1H, H–C4), 3.82–3.95 (m, 1H, H–C3), 3.99–4.06 (m, 2H, H–C5), 4.10 (dd, 1H, $J_{1,2}$ 10.3, $J_{1,2'}$ 4.3, H–C1); ^{13}C NMR δ 14.5 (($CH_3CH_2S)_2$-), 24.1 and 24.4 (($CH_3CH_2S)_2$-) 25.2 and 26.5 ($C(CH_3)_2$), 40.4 (C-2), 47.7 (C-1), 65.9 (C-5), 69.6 and 78.6 (C-3, C-4), 109.6 ($C(CH_3)_2$); MS (m/e) (relative intensity): 280 (3%, M^+), 219 (2, $M^+-C_2H_5S$), 201 (5, $C_{10}H_{17}O_2S^+$), 161 (15, $C_7H_{13}O_2S^+$), 131 (93, $C_6H_{10}OS^+$), 101 (11, $C_5H_9O_2^+$), 85 (26, $C_4H_5O_2^+$), 59 (100, $C_3H_7O^+$), 43 (32, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_3S_2$: C, 51.39; H, 8.63. Found: C, 51.29; H, 8.64.

*3.6.2.2. 4,5-*O*-Isopropylidene-*D*-lyxose diethyldithioacetal **25**.* R_f=0.34 (hexane:Et_2O, 1:1). $[\alpha]_D^{20}$=+22 (c 1.2, $CHCl_3$); ^{1}H NMR δ 1.29 and 1.30 (2t, each 3H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.39 and 1.45 (2s, each 3H, $C(CH_3)_2$), 2.47 (d, 1H, $J_{OH,2}$ 6.5, HO–C2, exchangeable with D_2O), 2.66 and 2.74 (2c, each 2H, J_{vic} 7.4, ($CH_3CH_2S)_2$), 2.77 (d, 1H, $J_{OH,3}$ 3.6, HO–C3, exchangeable with D_2O), 3.72–3.76 (m, 1H, H–C3, the signal turned into dd on addition of D_2O, $J_{3,2}$ 8.5, $J_{3,4}$ 3.2), 3.77–3.82 (m, 1H, H–C2, the signal turned into dd on addition of D_2O, $J_{2,1}$ 2.3, $J_{2,3}$ 8.5), 3.94 (dd, 1H, $J_{5,4}$ 7.0, J_{gem} 8.4, H–C5), 4.11 (dd, 1H, $J_{5',4}$ 6.7, J_{gem} 8.4, H′–C5), 4.28 (d, 1H, $J_{1,2}$ 2.3, H–C1), 4.42 (ddd, 1H, $J_{4,3}$ 3.2, $J_{4,5'}$ 6.7, $J_{4,5}$ 7.0, H–C4); ^{13}C NMR δ 14.5 and 14.6 (($CH_3CH_2S)_2$-), 25.2 and 26.4 ($C(CH_3)_2$), 25.7 and 25.9 (($CH_3CH_2S)_2$-), 54.7 (C-1), 66.4 (C-5), 71.1, 73.9 and 75.7 (C-2, C-3, C-4), 109.2 ($C(CH_3)_2$); IR (KBr, liquid film): 3495, 2995, 1460, 1385, 1375, 1215, 1160, 1065, 860, 795 cm^{-1}; MS (m/e) (relative intensity): 296 (3%, M^+), 235 (2, $M^+-C_2H_5S$), 217 (1, $C_{10}H_{17}O_3S^+$), 177 (19, $C_7H_{13}OS_2^+$), 161 (7, $C_7H_{13}O_4^+$), 135 (100, $C_5H_{11}S_2^+$), 75 (30, $C_3H_5S^+$), 59 (43, $C_3H_7O^+$), 43 (30, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_4S_2$: C, 48.62; H, 8.16. Found: C, 48.65; H, 8.17.

3.6.2.3. 4,5-O-Isopropylidene-D-xylose diethyldithioacetal ***26***. R_f=0.20 (hexane:Et_2O, 1:1); $[\alpha]_D^{20}$=+56.3 (c 0.25, $CHCl_3$); ^1H NMR δ 1.29 and 1.30 (2t, each 3H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.39 and 1.46 (2s, each 3H, $C(CH_3)_2$), 2.65 (d, 1H, $J_{OH,3}$ 7.8, HO–C3, exchangeable with D_2O), 2.64–2.81 (m, 4H, ($CH_3CH_2S)_2$-), 3.36 (d, 1H, $J_{OH,2}$ 2.8, HO–C2, exchangeable with D_2O), 3.51 (ddd, 1H, $J_{2,1}$ 8.8, $J_{2,OH}$ 2.8, $J_{2,3}$ 1.5, H–C2, the signal turned into dd on addition of D_2O, $J_{2,1}$ 8.8, $J_{2,3}$ 1.5), 3.86 (dd, 1H, $J_{5,4}$ 7.0, J_{gem} 8.1, H–C5), 4.01 (ddd, 1H, $J_{3,OH}$ 7.8, $J_{3,2}$ 1.5, $J_{3,4}$ 5.1, H–C3, the signal turned into dd upon addition of D_2O), 4.06 (d, 1H, $J_{1,2}$ 8.8, H–C1), 4.08 (dd, 1H, $J_{5',4}$ 6.5, J_{gem} 8.1, H–C5′), 4.28 (ddd, 1H, $J_{4,3}$ 5.1, $J_{4,5}$ 7.0, $J_{4,5'}$ 6.5, H–C4); ^{13}C NMR δ 14.4 and 14.5 (($CH_3CH_2S)_2$-), 24.0 and 25.7 (($CH_3CH_2S)_2$-), 25.5 and 26.5 ($C(CH_3)_2$), 55.3 (C-1), 66.1 (C-5), 70.3, 72.9 and 76.6 (C-2, C-3, C-4), 109.8 ($C(CH_3)_2$); IR (KBr, liquid film): 3425, 3000, 1450, 1385, 1210, 1165, 1080, 895, 810, 760 cm^{-1}; MS (m/e) (relative intensity): 296 (2%, M^+), 217 (2, $C_{10}H_{17}O_3S^+$), 177 (10, $C_7H_{13}OS_2^+$), 161 (12, $C_7H_{13}O_4^+$), 135 (100, $C_5H_{11}S_2^+$), 101 (25, $C_5H_9O_2^+$), 75 (27, $C_3H_5S^+$), 43 (42, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_4S_2$: C, 48.62; H, 8.16. Found: C, 48.62; H, 8.15.

3.6.3. To aldehyde ***19***

Following the above-described procedure for the addition of EETMS to compound **17**, starting from compound **19** (443 mg, 3.1 mmol) in THF (1 ml), EETMS (471 mg, 3.1 mmol) and *n*-BuLi (2.43 ml, 3.89 mmol), 960 mg (quantitative yield by ^1H NMR spectrum) of crude reaction were obtained. The crude reaction, without further purification, was treated with $LiAlH_4$ under two different experimental conditions:

3.6.4. Experiment A

The crude reaction (300 mg) was dissolved in THF (7 ml) and treated with $LiAlH_4$ (100 mg, 2.6 mmol) at 45°C, and stirred for 1 h. The above-described work-up led to a crude mixture containing compounds **29**, **30** and **31** in a 59:23:18 ratio (determined by integration of signals of H–C5 in the ^1H NMR spectrum of the crude reaction). Column chromatography using hexane:Et_2O (10:1) as the eluent afforded pure **29** (120 mg, 0.45 mmol, 46% yield) and a fraction (87 mg, 0.31 mmol, 32% yield) containing a mixture of compounds **30** and **31**. After subsequent flash chromatography (hexane:Et_2O, 15:1), pure **30** and **31** were obtained as colorless oils.

3.6.4.1. 2,3-Dideoxy-4,5-O-isopropylidene-D-glycero pentose diethyldithioacetal ***29***. R_f=0.25 (hexane:Et_2O, 1:1). $[\alpha]_D^{20}$=+12 (c 0.6, $CHCl_3$); ^1H NMR δ 1.26 (t, 6H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.35 and 1.41 (2s, each 3H, $C(CH_3)_2$), 1.73–2.03 (m, 4H, H–C2, H–C3), 2.53–2.72 (m, 4H, ($CH_3CH_2S)_2$-), 3.53 (dd, 1H, $J_{5,4}$ 6.7, J_{gem} 7.5, H–C5), 3.81 (dd, 1H, $J_{1,2}$=$J_{1,2'}$ 6.4, H–C1), 4.04 (dd, 1H, $J_{5',4}$ 6.0, J_{gem} 7.5, H′–C5) 4.02–4.13 (m, 1H, H–C4); ^{13}C NMR δ 14.5 (($CH_3CH_2S)_2$), 24.0 and 24.2 (($CH_3CH_2S)_2$-), 25.7 and 26.9 ($C(CH_3)_2$), 31.4 and 32.2 (C-2, C-3), 51.1 (C-1), 69.3 (C-5), 75.5 (C-4), 108.9 ($C(CH_3)_2$); IR (KBr, liquid film): 3010, 1455, 1385, 1375, 1220, 1155, 1065, 860, 790 cm^{-1}; MS (m/e) (relative intensity): 264 (19%, M^+), 249 (12, M^+-CH_3), 203 (19, $M^+-C_2H_5S$), 189 (17, $C_{19}H_{17}0_2S^+$), 145 (100, $C_7H_{13}OS^+$), 117 (34, $C_6H_{13}O_2^+$), 101 (64, $C_5H_9O_2^+$), 83 (43, $C_5H_7O^+$), 61 (11, $C_2H_5S^+$), 43 (35, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_2S_2$: C, 54.50; H, 9.15. Found: C, 54.68; H, 9.12.

3.6.4.2. (2R)-3-Deoxy-4,5-O-isopropylidene-D-glycero pentose diethyldithioacetal ***30***. R_f=0.60 (hexane:Et_2O, 1:1); $[\alpha]_D^{20}$=+52.4 (c 0.6, $CHCl_3$); ^1H NMR δ 1.21 and 1.22 (2t, each 3H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.30 and 1.36 (2s, each 3H, $C(CH_3)_2$), 1.85 (ddd, 1H, $J_{3,2}$ 8.2, J_{gem} 14.2, $J_{3,4}$ 8.2, H–C3), 1.99 (ddd, 1H, $J_{3',2}$ 3.0, J_{gem} 14.2, $J_{3',4}$ 4.6, H′–C3), 2.57–2.74 (m, 4H, ($CH_3CH_2S)_2$-), 3.34

(1H, d, $J_{OH,2}$ 2.4, HO–C2, exchangeable with D_2O), 3.55 (dd, 1H, $J_{5,4}$ 7.3, J_{gem} 8.1, H–C5), 3.80 (d, 1H, $J_{1,2}$ 5.6, H–C1), 3.82–4.07 (m, 1H, H–C2), 4.04 (dd, 1H, $J_{5',4}$, 6.0, J_{gem} 8.1, H′–C5), 4.25 (dddd, 1H, $J_{4,3}$ 8.2, $J_{4,3'}$ 4.6, $J_{4,5}$ 7.3, $J_{4,5'}$ 6.0, H–C4); ^{13}C NMR δ 14.5 and 14.6 (($CH_3CH_2S)_2$-), 25.1 and 25.8 (($CH_3CH_2S)_2$-), 25.8 and 26.9 ($C(CH_3)_2$), 36.9 (C-3), 57.7 (C-1), 69.5 (C-5), 72.1 and 74.7 (C-2, C-4), 109.2 ($C(CH_3)_2$); IR (KBr, liquid film): 3500, 3000, 1460, 1385, 1375, 1220, 1160, 1070, 870, 790 cm^{-1}; MS (m/e) (relative intensity): 280 (5%, M^+), 265 (5, M^+-CH_3), 262 (3, M^+-H_2O), 145 (40, $C_7H_{13}O_3^+$), 135 (100, $C_5H_{11}S_2^+$), 115 (15, $C_6H_{11}O_2^+$), 107 (28, $C_3H_7S_2^+$), 75 (56, $C_3H_7S^+$), 43 (36, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_3S_2$: C, 51.39; H, 8.63. Found: C, 51.29; H, 8.64.

*3.6.4.3. (2S)-3-Deoxy-4,5-*O*-isopropylidene-*D*-glycero pentose diethyldithioacetal* ***31***. R_f=0.67 (hexane:Et_2O, 1:1); $[\alpha]_D^{20}$=−42.6 (c 0.65, $CHCl_3$); ^{1}H NMR δ 1.28 (t, 6H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.37 and 1.42 (2s, each 3H, $C(CH_3)_2$), 1.73 (ddd, 1H, $J_{3',2}$ 9.9, J_{gem} 14.0, $J_{3',4}$ 4.5, H′–C3), 2.12 (ddd, 1H, $J_{3,2}$ 2.3, J_{gem} 14.0, $J_{3,4}$ 8.0, H–C3), 2.63–2.76 (m, 4H, ($CH_3CH_2S)_2$-), 2.95 (d, 1H, $J_{OH,2}$ 3.3, HO–C2, exchangeable with D_2O), 3.61 (dd, 1H, $J_{5,4}$ 7.1, J_{gem} 8.1, H–C5), 3.79 (d, 1H, $J_{1,2}$ 6.2, H–C1), 3.91 (m, 1H, H–C2, the signal turned into ddd on addition of D_2O, $J_{2,1}$ 6.2, $J_{2,3'}$ 9.9, $J_{2,3}$ 2.3), 4.12 (dd, 1H, $J_{5',4}$ 6.0, J_{gem} 8.1, H′–C5), 4.35 (dddd, 1H, $J_{4,3'}$ 4.5, $J_{4,3}$ 8.0, $J_{4,5}$ 7.1, $J_{4,5'}$ 6.0, H–C4); ^{13}C NMR δ 14.4 and 14.5 (($CH_3CH_2S)_2$-), 24.6 and 25.5 (($CH_3CH_2S)_2$-), 25.6 and 26.9 ($C(CH_3)_2$), 38.0 (C-3), 58.6 (C-1), 69.7 and 73.5 (C-2, C-4, C-5), 108.6 ($C(CH_3)_2$); IR (KBr, liquid film): 3500, 3000, 1460, 1385, 1375, 1220, 1160, 1070, 835, 790 cm^{-1}; MS (m/e) (relative intensity): 280 (3%, M^+), 265 (6, M^+-CH_3), 145 (38, $C_7H_{13}O_3^+$), 135 (99, $C_5H_{11}S_2^+$), 115 (20, $C_6H_{11}O_2^+$), 107 (37, $C_3H_7S_2^+$), 75 (100, $C_3H_7S^+$), 61 (23, $C_2H_5S^+$), 43 (26, $C_2H_3O^+$). Anal. calcd for $C_{12}H_{24}O_3S_2$: C, 51.39; H, 8.63. Found: C, 51.32; H, 8.68.

3.6.5. Experiment B

The crude reaction (650 mg) was dissolved in THF (14 ml), treated with $LiAlH_4$ (238 mg, 6.3 mmol) and refluxed for 1 h. The above-described work-up led to a residue which was purified by flash chromatography (hexane:Et_2O, 10:1) to yield pure **29** (392 mg, 1.5 mmol, 71%) as the only product.

3.7. Acetonation. General procedure[15c]

3.7.1. Of diol ***20***

To a solution of diol **20** (89 mg, 0.3 mmol) in C_6H_6 (2 ml), 2,2-dimethoxypropane (DMP, 0.074 ml, 0.6 mmol), and PTSA (0.85 mg, 4.30×10^{-3} mmol) were added. The mixture was refluxed for 30 min, and then the solvent was removed under reduced pressure. DMP (21×10^{-3} mg, 0.17 mmol) in C_6H_6 (1 ml) was subsequently added, the solvent was evaporated under reduced presssure, and the residue was treated with a saturated aqueous solution of $NaHCO_3$ (1 ml) and pentane (4 ml). The organic layer was washed with a saturated aqueous solution of NaCl, dried over Na_2SO_4, and the solvent removed under reduced pressure. The resulting crude reaction was purified by flash chromatography (hexane:Et_2O, 10:1) to afford pure **22** (97 mg, 97%) as a colorless oil.

*3.7.1.1. 2,3:4,5-Di-*O*-isopropylidene-*D*-ribose diethyldithioacetal* ***22***. R_f=0.47 (hexane:Et_2O, 4:1); $[\alpha]_D^{20}$=−121.6 (c 0.74, $CHCl_3$); ^{1}H NMR δ 1.28 and 1.29 (2t, each 3H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.34 (s, 6H, $C(CH_3)_2$), 1.42 and 1.49 (2s, each 3H, $C(CH_3)_2$), 2.63–2.84 (m, 4H, ($CH_3CH_2S)_2$-), 3.92 (dd, 1H, $J_{5,4}$ 5.6, J_{gem} 8.6, H–C5), 4.11 (dd, 1H, $J_{3,2}$ 6.5, $J_{3,4}$ 9.3, H–C3), 4.15 (dd, 1H, $J_{5',4}$ 6.2, J_{gem} 8.6, H′–C5), 4.28 (d, 1H, $J_{1,2}$ 4, H–C1), 4.56 (dd, 1H, $J_{2,1}$ 4, $J_{2,3}$ 6.5, H–C2), 4.64 (ddd, 1H, $J_{4,3}$ 9.3, $J_{4,5}$ 5.6, $J_{4,5'}$ 6.2,

H–C4); ^{13}C NMR δ 14.5 and 14.4 ((*C*H$_3$CH$_2$S)$_2$-), 24.7 (C(*C*H$_3$)$_2$ and CH$_3$*C*H$_2$S), 25.5 (CH$_3$*C*H$_2$S), 25.4, 26.5 and 26.8 (C(*C*H$_3$)$_2$), 50.2 (C-1), 68.31 (C-5), 73.2, 76.7 and 81.3 (C-2, C-3, C-4), 109.2 and 109.7 (*C*(CH$_3$)$_2$); IR (KBr, liquid film): 3000, 1455, 1385, 1255, 1215, 1160, 1070, 855 cm^{-1}; MS (m/e) (relative intensity): 336 (8%, M$^+$), 263 (3, C$_{11}$H$_{19}$O$_3$S$_2^+$), 217 (22, C$_{10}$H$_{17}$O$_3$S$^+$), 177 (6, C$_6$H$_9$O$_2$S$_2^+$), 135 (100, C$_5$H$_{11}$S$_2^+$), 101 (34, C$_5$H$_9$O$_2^+$), 87 (53, C$_4$H$_7$O$_2^+$), 85 (32, C$_4$H$_5$O$_2^+$), 43 (100, C$_2$H$_3$O$^+$). Anal. calcd for C$_{15}$H$_{28}$O$_4$S$_2$: C, 53.53; H, 8.39. Found: C, 53.49; H, 8.41.

*3.7.2. Of crude reaction of diols **20** and **21***

To a solution of crude reaction containing diols **20** and **21** (178 mg, 0.6 mmol) in C$_6$H$_6$ (4 ml), DMP (0.15 ml, 1.2 mmol) and PTSA (1.7 mg, 8.6 mmol) were added following the above-described procedure for the acetonation of compound **20**. Work-up led to a crude mixture (200 mg) containing **22**:**23** in a 88:12 ratio determined by ^{1}H NMR (H–C5). Column chromatography using hexane:Et$_2$O (25:1) as the eluent, afforded pure **22** and **23** as colorless oils.

*3.7.2.1. 2,3:4,5-Di-*O*-isopropylidene-*D*-arabinose diethyldithioacetal, **23**.* R$_f$=0.42 (hexane:Et$_2$O, 4:1); [α]$_D^{20}$=+102 (c 0.57, CHCl$_3$); ^{1}H NMR δ 1.26 and 1.28 (2t, each 3H, J$_{vic}$ 7.4, (C*H*$_3$CH$_2$S)$_2$-), 1.34, 1.38, 1.42 and 1.45 (4s, each 3H, C(*C*H$_3$)$_2$), 2.67–2.80 (m, 4H, (CH$_3$C*H*$_2$S)$_2$-), 3.96 (dd, 1H, J$_{5,4}$ 4.2, J$_{gem}$ 8.3, H–C5), 4.03 (d, 1H, J$_{1,2}$ 2.6, H–C1), 4.05–4.16 (m, 3H, H–C3, H–C4 and H′–C5), 4.29 (dd, 1H, J$_{2,1}$ 2.6, J$_{2,3}$ 6.9, H–C2); ^{13}C NMR δ 14.3 and 14.4 ((*C*H$_3$CH$_2$S)$_2$-), 24.9 and 25.2 ((CH$_3$*C*H$_2$S)$_2$-), 26.6, 27.1, 27.3 and 28.3 (C(*C*H$_3$)$_2$), 52.3 (C-1), 67.7 (C-5), 77.1, 79.1 and 84.4 (C-2, C-3, C-4), 109.7 and 110.2 (*C*(CH$_3$)$_2$); IR (KBr, liquid film): 3000, 1460, 1385, 1375, 1220, 1160, 1070, 890, 855 cm^{-1}; MS (m/e) (relative intensity): 336 (10%, M$^+$), 263 (4, C$_{11}$H$_{19}$O$_3$S$_2^+$), 217 (27, C$_{10}$H$_{17}$O$_3$S$^+$), 177 (4, C$_6$H$_9$O$_2$S$_2^+$), 135 (73, C$_5$H$_{11}$S$_2^+$), 101 (30, C$_5$H$_9$O$_2^+$), 87 (32, C$_4$H$_7$O$_2^+$), 85 (27, C$_4$H$_5$O$_2^+$), 43 (100, C$_2$H$_3$O$^+$). Anal. calcd for C$_{15}$H$_{28}$O$_4$S$_2$: C, 53,53; H, 8.39. Found: C, 53.51; H, 8.43.

*3.7.3. Of diol **25***

Following the above-described procedure for the acetonation of compound **20**, starting from compound **25** (32.2 mg, 0.11 mmol) in C$_6$H$_6$ (1 ml), DMP (0.027 ml, 0.22 mmol), and PTSA (0.31 mg, 1.61×10^{-3} mmol), compound **27** (19 mg, 0.055 mmol, 50% yield) was obtained as a colorless oil after flash chromatography using hexane:Et$_2$O (15:1) as the eluent.

*3.7.3.1. 2,3:4,5-Di-*O*-isopropylidene-*D*-lyxose diethyldithioacetal **27**.* R$_f$=0.35 (hexane:Et$_2$O, 4:1); [α]$_D^{20}$=−35 (c 0.33, CHCl$_3$); ^{1}H NMR δ 1.28 (t, 6H, J$_{vic}$ 7.4, (C*H*$_3$CH$_2$S)$_2$-), 1.36, 1.38, 1.44 and 1.54 (4s, each 3H, C(CH$_3$)$_2$), 2.61–2.92 (m, 4H, (CH$_3$C*H*$_2$S)$_2$-), 3.85 (dd, 1H, J$_{5,4}$ 8.1, J$_{gem}$ 7.8, H–C5), 4.05 (dd, 1H, J$_{5',4}$ 6.3, J$_{gem}$ 7.8, H′–C5), 4.14 (dd, 1H, J$_{3,2}$ 5.7, J$_{3,4}$ 3.0, H–C3), 4.21 (d, 1H, J$_{1,2}$ 10.0, H–C1), 4.26 (dd, 1H, J$_{2,1}$ 10.0, J$_{2,3}$ 5.7, H–C2), 4.56 (ddd, 1H, J$_{4,3}$ 3.0, J$_{4,5}$ 8.1, J$_{4,5'}$ 6.3, H–C4); ^{13}C NMR δ 14.2 and 14.4 ((*C*H$_3$CH$_2$S)$_2$-), 24.0 and 24.8 ((CH$_3$*C*H$_2$S)$_2$), 25.3, 25.8, 26.5 and 26.7 (C(*C*H$_3$)$_2$), 49.6 (C-1), 66.4 (C-5), 73.7, 76.4 and 79.0 (C-2, C-3, C-4), 109.0 and 109.6 (*C*(CH$_3$)$_2$); IR (KBr, liquid film): 3000, 1460, 1385, 1260, 1220, 1160, 1070, 885 cm^{-1}; MS (m/e) (relative intensity): 336 (3%, M$^+$), 321 (4, M$^+$−CH$_3$), 278 (4, C$_{12}$H$_{22}$O$_3$S$_2^+$), 217 (27, C$_{10}$H$_{17}$O$_3$S$^+$), 177 (31, C$_6$H$_9$O$_2$S$_2^+$), 135 (100, C$_5$H$_{11}$S$_2^+$), 101 (59, C$_5$H$_9$O$_2^+$), 87 (55, C$_4$H$_7$O$_2^+$), 85 (49, C$_4$H$_5$O$_2^+$), 59 (58, C$_3$H$_7$O$^+$), 43 (98, C$_2$H$_3$O$^+$). Anal. calcd for C$_{15}$H$_{28}$O$_4$S$_2$: C, 53.53; H, 8.39. Found: C, 53.62, H; 8.36.

3.7.4. Of diol ***26***

Following the above-described procedure for the acetonation of compound **20**, starting from compound **26** (32.5 mg, 0.11 mmol) in C_6H_6 (1 ml), DMP (0.027 ml, 0.22 mmol), and PTSA (0.31 mg, 1.61×10^{-3} mmol), compound **28** (17 mg, 0.051, 46% yield) was obtained as a colorless oil after flash chromatography using hexane:Et_2O (15:1) as the eluent.

*3.7.4.1. 2,3:4,5-Di-*O*-isopropylidene-*D*-xylose diethyldithioacetal* ***28***. R_f=0.36 (hexane:Et_2O, 4:1); $[\alpha]_D^{20}$=−55.1 (c 0.33, $CHCl_3$); ^{1}H NMR δ 1.27 and 1.28 (2t, each 3H, J_{vic} 7.4, ($CH_3CH_2S)_2$-), 1.38 (s, 3H, $C(CH_3)_2$), 1.44 (s, 6H, $C(CH_3)_2$) and 1.47 (s, 3H, $C(CH_3)_2$), 2.66–2.85 (m, 4H, ($CH_3CH_2S)_2$-), 3.91 (d, 1H, $J_{1,2}$ 5.2, H–C1), 3.92 (dd, 1H, $J_{5,4}$ 7.5, J_{gem} 8.0, H–C5), 4.06 (dd, 1H, $J_{5',4}$ 6.7, J_{gem} 8.0, H′–C5), 4.15 (dd, 1H, $J_{3,2}$ 7.4, $J_{3,4}$ 3.2, H–C3), 4.34 (dd, 1H, $J_{2,1}$ 5.2, $J_{2,3}$ 7.4, H–C2), 4.34 (ddd, 1H, $J_{4,3}$ 3.2, $J_{4,5}$ 7.5, $J_{4,5'}$ 6.7, H–C4); ^{13}C NMR δ 14.3 and 14.4 (($CH_3CH_2S)_2$-), 24.9 and 25.3 (($CH_3CH_2S)_2$-), 25.6, 26.1, 27.2 and 27.4 ($C(CH_3)_2$), 53.0 (C-1), 65.9 (C-5), 75.3, 78.7 and 80.0 (C-2, C-3, C-4), 109.8 and 110.1 ($C(CH_3)_2$); IR (KBr, liquid film): 3000, 1455, 1380, 1370, 1225, 1160, 1075, 995, 885 cm^{-1}; MS (m/e) (relative intensity): 336 (6%, M^+), 217 (5, $C_{10}H_{17}O_3S^+$), 177 (4, $C_6H_9O_2S_2^+$), 135 (81, $C_5H_{11}S_2^+$), 101 (56, $C_5H_9O_2^+$), 87 (32, $C_4H_7O_2^+$), 85 (33, $C_4H_5O_2^+$), 59 (43, $C_3H_7O^+$), 43 (100, $C_2H_3O^+$). Anal. calcd for $C_{15}H_{28}O_4S_2$: C, 53,53; H, 8.39. Found: C, 53.58; H, 8.38.

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